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Harold J. Wiesner

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PLATING ON DIFFICULT-TO-PLATE METALS: WHAT'S NEW?*

Harold J. Wiesner
Lawrence Livermore National Laboratory, University of California
Livermore California 94550

This paper surveys some of the changes since 1970 in procedures for plating on such materials as titanium, molybdenum, silicon, aluminum, and gallium arsenide. While basic procedures for plating some of these materials were developed as many as 30 to 40 years ago, changes in the end uses of the plated products have necessitated new plating processes. In some cases, vacuum techniques--such as ion bombardment, ion implantation, and vacuum metallization--have been introduced to improve the adhesion of electrodeposits. In other cases, these techniques have been used to deposit materials upon which electrodeposits are required.

INTRODUCTION

"Difficult-to-plate" metals is a relative term: it depends on where one is in the process of developing a satisfactory plating procedure for a particular application. Today a metal may be easy to plate on because the investigators have found the correct sequence of operations. Perhaps a year later the same process will be unsatisfactory for plating on a new alloy of the same metal that an engineer wishes to use because of its superior strength or other mechanical properties. Thus, the changing technology creates new "difficult-to-plate" metals and alloys. For example, we are all familiar with the exponential growth of the electronics industry, which has also created a myriad of plating problems. We shall hear several papers dealing with these problems and how they were solved.

One industry that has had to deal with some very difficult plating problems is the nuclear energy industry. Vast sums of money have been spent in learning how to coat the metals and alloys used in nuclear energy: uranium, beryllium, thorium, tantalum, tungsten, zirconium, and niobium. Electroplating

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has contributed to the engineering performance of these materials by providing metal coatings of low neutron cross section, corrosion-resistant metals, and methods of joining dissimilar materials that are impossible to weld or braze.

Plating procedures for some of these metals and alloys have existed for 20 to 30 years,¹ but the latest technology will be described at this conference. I have chosen not to cover all of the metals and alloys in the "difficult-to-plate" category, since this would require a long chapter or a book. Rather, my talk will be confined to a discussion of plating on titanium, molybdenum, silicon, aluminum, and gallium arsenide.

Since Beach and Faust¹ covered a large number of these materials during the period between 1950 and 1970, this talk will extend the literature, within the limitations mentioned above, from 1970 to 1980.

REQUIREMENTS FOR PLATING ON DIFFICULT-TO-PLATE METALS

Electroplating on these materials has the same fundamental requirements as does electroplating on the more frequently plated metals and alloys. The surface must be reasonably smooth, clean, active for accepting an electroplate, but not reactive with the plating solution. The distinguishing feature of the metals and alloys mentioned above, however, is that they are either very active or chemically passive in the aqueous solutions that are well established for the common metals. The surface metallurgy approach, then, provides guidance in choosing the best coating or coatings for an unusual metal. One must not only be concerned with the physical and chemical cleanliness of the surface to be electroplated but also with the mechanical cleanliness--the freedom from a stressed, smeared, or torn surface. Disturbed surfaces can contribute greatly to the lack of adhesion of electrodeposits.

Of equal importance in selecting a coating process is a knowledge of the properties of diffusion alloys that may be formed. Such alloys may be beneficial in improving adhesion of the plated layers, or they may be detrimental if brittle and weak phases are formed during a high-temperature application.

CHOICE OF ELECTRODEPOSITS

To a large extent, the end use of the electroplated metal or alloy governs the choice of the plated coating. In reactors, for example, only metals of low neutron cross section, such as tin, lead, bismuth, and aluminum are useful for coatings thicker than about 250 μm .¹ In gaseous diffusion apparatus, heavy deposits of nickel have been used to provide resistance to corrosion.

The main consideration in choosing coatings for high-temperature applications are 1) the alloying characteristics with the basic metal and 2) the permeability of oxygen or other gases that may react with the substrate after diffusing through the coating. Thus, for high-temperature materials, only coatings resistant to oxidation and to diffusion of oxygen through them can be used. These include nickel, cobalt, chromium, rhodium, gold, rhenium, and certain of their alloys.

In titanium landing gear for aircraft, resistance to abrasion and to corrosion by salt water are important requirements. Heavy chromium deposits have been successfully used in this application.

In chromium-plating aluminum landing gear, the copper strike had to be eliminated because of the cracks in the chromium that could create large potential differences and lead to early stress corrosion cracking of the aluminum.

ADHESION AND OTHER TESTS OF ELECTRODEPOSITS

As one goes through the excellent chapter of Beach and Faust, one striking omission is a lack of data dealing with the bond strength of the electrodeposited coatings to the basis metals. While it is possible that heat tests, bend tests, and chisel testing were done, these data fail to appear except in the section dealing with zirconium. There, the heat treat, temperature, and time relationship to the bond of the nickel plate are given as poor, fair, and good.

In contrast, the paper of Dini and Johnson² to be given at this conference will reflect a marked difference. Ring shear testing and conical head tensile testing data give quantitative information on the effect of variables upon the adhesion of the electrodeposits to the substrates. For example, in plating on beryllium, when the pH of the zincate solution was within the range of 3.0 to 7.7, shear strength values of 232 to 281 MN/m² (33.8 to 40.8 ksi) were obtained. However, if the pH was raised to 9.3 to 10.7, shear strength fell to 26 to 51 MN/m² (3.8 to 7.4 ksi). Tensile testing of samples done under the optimum plating procedure showed a tensile strength of 171 MN/m² (24.8 ksi). The break was in the beryllium.

The trend towards meaningful tests that give semiquantitative to quantitative data is increasing. The problem is complicated, however, since the end-product usage determines the type of testing done. In one case heat cycling may give meaningful information. In another application with the same coating on the same basis metal, a different type of test may be more applicable. Translation of the test information from one application to the other is then not possible.

PLATING ON TITANIUM

Because of the high strength-to-weight ratio of titanium and its alloys, titanium has been used in a number of aircraft applications. The well-known galling effect of titanium against other metals and alloys has necessitated coatings of some type. Typically, these coatings are chromium plating or electroless nickel for wear-resistant applications. Beach and Faust¹ describe five general procedures for activating titanium for electroplating: anodic etching, zinc strike-plating in glycol fluoride solutions,³ chemical etching in chromic-hydrofluoride solutions,^{4,5} electrolytic activation with alternating current in acetic-hydrofluoric acid solutions,⁴ chemical etching in hot hydrochloric acid solutions,⁶ and vapor-blasting of the titanium plus heat-bonding of the plated coating.⁷ Harding⁸ and others have used vapor-blasting plus electroless diffused nickel to obtain a good bond.

Recently, Turns et al.⁹ have developed the following process: wiping the part with cheesecloth moistened with trichloroethylene; vapor-degreasing; grit-blasting titanium alloys with 120 mesh Al_2O_3 ; etching in solutions containing 20 vol% nitric acid plus 20 wt% sodium citrate at 70°C for 5 min; alkaline electroless nickel-plating for 1 hr at 90°C; rinsing with tap water; and drying in compressed air.

The deposits were tested by conventional bend tests, Falex seizure tests, Frictionometer tests, notched sustained-load tests, and compact tension tests. Deposits in the range of 3.8 to 12.7 μm (0.000125 to 0.0005 in.) passed the adhesion test whereas thicker deposits failed.

After the specimens were electroless nickel-plated, they could be chromium-plated by the following process: scrubbing all areas with a paste of

pumice and 50% HCl; rinsing quickly in tap water; Wood's nickel-striking for 2 min at 15.5 A/dm^2 (1 A/in.^2); rinsing in tap water; transferring to a room-temperature copper cyanide strike for 2 min at 5 to 6 V; rinsing quickly; transferring the specimen to a chromium plating solution and plating to the required thickness; and finishing mechanically or grinding to the final dimensions.

Dini and Johnson¹⁰ ran ring shear tests for a number of activation procedures used to plate nickel on titanium. Values ranging from 25 to 266 MN/m^2 (3.6 to 43.3 ksi) were obtained.

Hartshorn¹¹ claimed a method of depositing nickel or chromium onto titanium or zirconium by coating the surface prior to plating with an extremely thin fluoroborate or silicate conversion layer. In another reference¹² Hartshorn claims to be plating over a titanium hydride film. Ruben¹³ also patented a process for plating nickel on titanium that involved the electrolytic formation of titanium hydride. Winfree¹⁴ found that smooth adherent nickel deposits could be achieved by using a controlled half-wave anodic etch in a quiescent acid to produce selective keyholing of the substrate surface, followed by cathodically applied nickel plating.

Augustine,¹⁵ on the other hand, prepared the titanium or titanium-alloy substrate for plating using a chromic acid/sulfuric acid solution. Ferat et al.¹⁶ found it necessary to use ionic bombardment (sputtering of iron or copper) to achieve adhesion. Once the iron or copper was deposited by sputtering, conventional electroplating procedures could be used.

Titanium honeycomb panel structures¹⁷ were prepared for plating by first being cleaned by immersion (1 to 5 min) in a nonaqueous solution of chromic and sulfuric acids. The honeycomb was then descaled by being anodically

treated for 5 to 10 min in a mixture of solutions of acetic, sulfuric, and hydrofluoric acids. Copper or carbon was used for the cathodes.

It is clear that a number of procedures have been developed for plating onto titanium and its alloys. How good they are can only be determined by testing in a uniform manner. Dini and Johnson¹⁸ have done this by obtaining samples from a number of sources, and they will be reporting these results at this conference.

A relatively recent patent issued to S. Fujishiro and D. Eylon¹⁹ makes use of ion implantation to saturate the surface of titanium with ions of a noble metal or noble alloy. The impingement of the metallic ions is continued until an oxidation-resistant surface is obtained. The entire process requires 2 to 5 min. This technique opens up an entirely new supplemental area to the electroplater.

Winters²⁰ studied selective gold plating on palladium-titanium conductor patterns from buffered potassium cyanide solutions. He found that gold is deposited on titanium at a potential 200 mV more negative than that of palladium. This potential difference can be used to selectively nucleate gold on palladium patterns over titanium.

The marriage of vacuum techniques with electroplating is abundantly evident in the electronics field. However, Kemmerer and Mills²¹ studied the metallization conditions necessary to reduce the amount of gold. They found this was possible by development of a titanium-copper-nickel-gold metallization.

On large titanium parts Hirsch²² studied a number of processes for coating 6Al-2Sn-6V, 6Al-4V, 6Al-6Mo-2Sn-4Zn, and 6Al-1Cu-4Mo-5Zn titanium alloy gear boxes to withstand 126×10^6 repetitive stress cycles at a

contact stress of 13.2×10^4 psi. Iron-plated coatings, diffusion-bonded to the titanium core and then carbo-nitrided, were selected as the most satisfactory system.

Eckler and Manty²³ studied pulse plating as well as direct plating of chromium-molybdenum alloys onto titanium alloys. They found the wear-resistant properties of the chromium-molybdenum alloy to be superior to straight chromium plating.

PLATING ON MOLYBDENUM

Although molybdenum has desirable high-temperature strength, it oxidizes catastrophically in air at temperatures above 980°C . Since chromium and molybdenum diffuse to form a solid solution with good physical properties, chromium plating was chosen as the initial layer in early work. Anodic activation of the molybdenum surface was accomplished in mixtures of acids such as sulfuric-phosphoric acid and chromic-sulfuric acid. Activation times varied from 20 to 180 s. Once the chromium layer was deposited, subsequent layers of other metals could readily be electrodeposited.

Gold has been electrodeposited directly onto molybdenum²⁴ by first applying a thin gold coating that is then heated to 1200 to 1370°C . Thereafter, gold can be built up if necessary.

A second process²⁵ involves ion plating about 1000 Å (100 nm) of gold then electroplating to the desired thickness. Excellent adhesion is obtained. Plating on metallized ceramics for the electronics industry involves specialized procedures, which we shall hear about at this conference.

Asher and Keller²⁶ developed a barrel-plating process for plating nickel onto molybdenum.

PLATING ON SILICON

Mehl et al.²⁷ described a method of plating gold onto silicon using a bath containing 2.7 g/l $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in an aqueous solution containing 50% HF by volume. The silicon was etched or cleaned in boiling chloroform. The sample was then immersed in the gold solution and etched anodically for 15 s at 2 mA/cm^2 . After being rinsed thoroughly in distilled water, the silicon was gold-plated for 30 s at 4 A/cm^2 in a standard gold cyanide solution. It was then rinsed again, dried, and heated 30 s to 400°C in flowing hydrogen.

Electroless nickel has been plated on silicon using the following process²⁸: mechanical polishing of the silicon surface; chemical etching in HNO_3 -HF- H_2O ; rinsing; chemical etching in 48% HF for 10 s; rinsing; and plating in an alkaline electroless nickel solution at 93 to 96°C .

While these earlier processes were developed for plating on silicon, the majority of silicon chips for electronic applications today are plated using vacuum techniques. After the silicon is cleaned and etched, aluminum is evaporated onto it. A glass coating is then laid down followed by more evaporated aluminum. Nickel and gold may then be electroplated.

Hentzschel²⁹ prepared silicon surfaces for electroless nickel by activation with an aqueous hydrofluoric acid solution containing from 1 to 100 ppm of ionic gold.

Garceau and Johnson³⁰ described a method of holding silicon beam-lead integrated circuits during electroplating without damage. The backsides of the wafers are held vertically on tubular cathode contacts and silicon-rubber gaskets. Velocity plating is then begun by forcing the plating solution through a diffuser at the anode.

PLATING ON ALUMINUM

I must confess that I had a hard time placing aluminum in the category of "difficult-to-plate" metals. As you can see from Table 1 (taken from Schardein³¹), processes for plating on aluminum have been around for a long time with commercial plating installations in existence for at least 35 years.

Table 1. Plating processes for aluminum.

First patent	1896	England
Immersion tin	1903	England
Immersion tin	1904	France
Immersion tin	1915	U.S.
Zincate	1927	U.S. Pat. 1,627,000
Phosphoric anodize	1934	Fisher process
Oxalic anodize	1934	Krome alum process
Double zincate	1939	U.S. Pat. 2,142,564
Stannate	1965	Alstan process

However, rather than alienate five authors and a co-chairman, I have attempted to bring the literature up to date from about 1970 and to discuss the trends. One trend that is apparent is the attempt to plate on aluminum and its alloy directly with electroless as well as electrolytic coatings.

Direct Plating on Aluminum. Asada³² used alternating current in a solution containing nickel ions to produce a layer of aluminum oxide plus nickel oxide. He then reduced the film cathodically, followed by nickel plating. Petit et al.³³ plated electroless nickel onto a variety of aluminum alloys by the following process: degreasing and cleaning in sulfuric acid containing 39 g/l potassium dichromate; dipping in 50 g/l sodium hydroxide; etching in a solution containing 640 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 100 ml/l of

85% lactic acid; dipping in 1:1 nitric acid 2 to 3 min; desmutting in a solution containing 2 to 5 ml 48% HF in 8N HNO_3 ; dipping in an activation solution containing 25 g/l sodium hypophosphite and 25 ml/l of ammonium hydroxide at 50°C; catalytic nickel-striking for 1 min at 85 to 90°C in a solution containing 25 g/l ammonium citrate (the pH of this solution was adjusted to 9.0 to 9.5 with ammonium hydroxide); and, without rinsing, transferring the specimen quickly to the electroless nickel bath.

Coll-Palagos³⁴ patented a process in which aluminum and its alloys can be electrolessly plated by degreasing, cleaning, and etching with HF followed by immersion in an acidic electroless plating solution containing nickel ions, hypophosphite ions, fluoroborate and/or sulfamate ions, glycollate ions, and a small number of fluoride ions. The pH was within the range of 5.3 to 7.

In a somewhat similar approach, Bellis³⁵ used a fluoride solution containing nickel, iron, or silver prior to depositing nickel from an amine borane bath.

Hansson³⁶ patented a somewhat similar process for plating nickel, copper, tin, zinc, and cadmium onto aluminum wire. Donakowski and Morgan were recently issued three patents³⁷⁻³⁹ for a method of cleaning, activating, and plating 7000-series aluminum bumpers using a brass strike. The pretreatment cycle is shown in Table 2. Donakowski and Morgan point out that the process described is only suitable for 7000-series aluminum parts.

Table 2. Brass strike pretreatment cycle.

Operation	Time	Temperature
Buff and soak	---	---
Soak clean	2 min	160-180 °F
Water rinse	30 s	Warm
Soak in electrocleaner	30 s	120-140 °F
Water rinse	30 s	Warm
Acid dip	30 s	Room temperature
Water rinse	30 s	Warm
Brass strike 7-9V, 30 A/m ²	2-5 min	Room temperature

The composition of the brass strike solution is given in Table 3.

Table 3. Brass strike solution composition.

Copper cyanide (as copper)	18 g/l (2.4 oz/gal)
Zinc cyanide (as zinc)	12 g/l (1.6 oz/gal)
Free sodium cyanide	48 g/l (6.4 oz/gal)
Sodium hydroxide	15 g/l (2.0 oz/gal)
Cathode current density	215-490 A/m ² (20-45 A/ft ²)
Anode current density	160-320 A/m ² (15-30 A/ft ²)
Voltage	7-9 V
Temperature	20-32°C (68-90 °F)
Brass anodes	52% copper, 46% zinc

Vranty⁴⁰ developed a process for pretreating an aluminum body prior to electroless deposition of nickel patterned with a mask and having Al₂O₃ present. This process consisted of: cleaning; exposing the specimen to a stop-etchant that removes only Al₂O₃ and simultaneously activates the surface for deposition of nickel; and (without rinsing) immersing the specimen in nickel to further activate the aluminum for subsequent deposition of nickel.

Immersion Pretreatments--Zinc. An excellent literature review of immersion-deposit pretreatments for electroplating on aluminum was published by Lashmore⁴¹ as a part of AES Project 41. The same author⁴² has studied the morphology of zinc pretreatments on pure aluminum as well as on the alloys.

In a 97% alloy containing magnesium and iron as impurities, the zinc deposited principally at the grain boundaries. The zincate solution contained

525 g/l NaOH, 100 g/l ZnO, 1 g/l of ferric chloride, and 10 g/l Rochelle salts. When 99.999% pure aluminum was treated similarly, the orientation of the zinc at the grain boundaries did not occur.

Using helium backscatter data, Lashmore has shown that when 99.999% pure aluminum is zincated in the above solution for 60 s and then dipped in nitric acid for 20 s, the zinc concentration on the surface is still about 2 monolayers thick. Iron was also present in a concentration of 1.5×10^{15} atoms/cm². It appears, therefore, that a zinc-iron alloy is formed.

In a practical application of the use of a zinc-immersion treatment, Klinglenmaier⁴³ described the process of hard iron-plating of aluminum pistons for the Vega engine. Over five million pistons were plated in production with excellent results.

Kampert⁴⁴ and Kampert, Cochran, and Baker⁴⁵ have pointed out that in many environments the zinc film is anodic to both the electrodeposited coating as well as to the aluminum substrate. Thus, if the electroplate is ruptured to the basis metal, undermining corrosion can occur. To avoid this difficulty, Alcoa developed a new process (Alcoa 661) in which the copper cyanide strike was eliminated and replaced with a neutral nickel solution. The zincated aluminum is placed in the nickel bath, and when the potential (measured against a nickel electrode) drops approximately 200 mV below the original potential, nickel plating is started. Galvanic displacement of the nickel from solution by zinc continues until the zinc deposit substantially disappears. Typically, this may require 2 min.

Immersion Processes--Tin. The immersion process that uses tin plus bronze for plating on aluminum was introduced much later than the immersion-zinc or the phosphoric-acid anodizing processes. Recent tests⁴⁶ have shown this process to have less tendency for undermining and blistering of electrodeposited decorative nickel-chromium coatings on aluminum when compared to other plating processes. In an earlier study, Jongkind⁴⁷ reported on a comparison of the zincate and stannate immersion processes using X-7046 aluminum bumper bar stock plated with bright copper, nickel, and chromium. The zincate process showed lateral corrosion at the interface between the basis metal and plated layers. In the original process the stannate solution contained copper cyanide and free cyanide, but a recent patent⁴⁸ shows only potassium stannate, along with certain organic activators.

Toth and Walker⁴⁹ received a patent for plating on aluminum using an immersion-tin deposit from a stannate solution containing a chelating agent prior to copper plating.

Aluminum bus bars are plated with tin or silver⁵⁰ using the Alstan 80* process. However, one of the weaknesses of the Alstan 80 process from the standpoint of conveyor operation is that the transfer time from the stannate solution to the bronze strike is relatively short (10 to 15 s). Schardein⁵¹ reports that the process has been modified to allow transfer times of up to 1 min.

*Trademark of M T Chemicals, Inc.

Phosphoric Acid Anodizing. As shown in Table 1, phosphoric acid anodizing as a pretreatment for plating on aluminum has existed since 1934. However, it has not achieved great acceptance because it is alloy-sensitive. Therefore, a consistent coating thickness and large pore diameter of the anodized film are not always achieved. Shardein⁵¹ has recently reported that consistent results have been obtained with 7029 and 7046 alloys by operating with a 25 vol% phosphoric solution and by carefully controlling the bath temperature and operating current density. Wittrock,⁵² on the other hand, has patented a process that requires a high current density initially (within 30 s from the start of anodizing). The current density is then allowed to decay to a level between 150 and 500 A/cm².

Tremmel et al.⁵³ patented a mixed solution containing phosphoric, sulfuric, and acetic acids for anodizing the 7000-series alloys prior to plating. In a recent article, Lashmore⁵⁴ has discussed the state of the art of plating on anodized aluminum.

Nguyen and Foley⁵⁵ studied the mechanism of pitting of aluminum.

GALLIUM ARSENIDE

Weller and Wen⁵⁶ in 1971 reported upon a procedure for fabricating small avalanche diodes of either silicon or gallium arsenide. They used a novel electrochemical etching technique plus plating of a copper heat-sink block. They stated that the etching technique provided improved uniformity and thickness control. Wafers 6 μ m thick and over 1.5 cm in diameter have been fabricated reproducibly. Wrixon et al.⁵⁷ fabricated Schottky-barrier type diodes for use at millimeter wavelengths. They used cross stripes of 0.25- and 0.4- μ m widths fabricated on gallium arsenide. The junctions were formed by

electroplating gold through the cross-shaped cuts. This shaping of the diode resulted in a 30% reduction in spreading resistance over that of photolithographically formed circular diodes. Wrixon and Kelly⁵⁸ fabricated ohmic contacts on N-type gallium arsenide by alloying electroplated layers of gold-tin-nickel-gold at 300°C. Dasaro et al.⁵⁹ fabricated gallium arsenide mesfets with reduced inductance via connections to source electrodes. This was accomplished by etching, electroless gold-plating, and electroplating. The short gold-plated source connections reduce the common lead parasitic inductance by a large factor, resulting in a gain increase of 2 dB at 4 GHz.

McGuire et al.⁶⁰ studied the diffusion of gold through thin films of electroplated platinum using Auger electron spectroscopy. Platinum is widely used for the Schottky-barrier metallization on gallium arsenide IMPATT varactor diodes, with gold being used to contact the platinum. If gold diffused through the platinum into the active semiconductor region, long-term reliability for diodes operating at elevated temperatures could be affected. Diffusion anneals were carried out in the range of 750 to 900 K in an ultrahigh vacuum system. Auger spectroscopy monitored the surface compositional changes. From the data collected, a grain-boundary mechanism is proposed for the diffusion of gold through the platinum, and the effective grain-boundary diffusion constant for gold in thin platinum films is given.

SUMMARY

We have presented an overview of some of the developments since 1970 in plating on difficult-to-plate metals. The metals discussed here have included only those discussed at this conference.

Increasing use of these metals in a variety of applications in the nuclear, aircraft, aerospace, and electronics industries has necessitated a number of new plating procedures to meet special requirements. Probably the most significant change has been the introduction of such vacuum techniques as ion bombardment, ion implantation, and vacuum plating in conjunction with electroplating to produce, in some cases, better adhesion, and, in other cases, products that could not be produced by electroplating alone.

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